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## **Chapter 6**

### **Clinker Burning Behaviour of Heavy Metals**



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## **1. INTRODUCTION**

For hundreds of millions of years the heavy toxic metals remained buried in the ground in non-soluble forms, mainly as oxides and sulphides, and as such were not a pollutant of the biosphere. The use of metals by man started about 6000 B.C. when natural metallic gold, silver and copper supplemented the use of stone, bone and wood. Between 4500 and 3500 B.C. the discovery that metals such as copper could be extracted from native ores, made malleable by heat and mixed with other metals to form alloys, formed the basis of the vast metal industries of today. Accompanying this came potential hazards to health.

The early ores were mined from pits without adequate ventilation and resulted in an exposure to dusts and fumes whose composition was unknown and whose toxicity was on the whole not even suspected. Strabo, in describing the arsenic mines in Pontus, however reported:

*"the air in the mines is both deadly and hard to endure on account of the grievous odour of the ore, so the workmen are doomed to a quick death".*

From the early beginnings modern technology has made available metals whose toxic properties were first realised after incidents of ill-health or death caused by inhalation of dust and fume or by contact with the skin. Such metals include beryllium, selenium, cadmium, gallium, indium, etc. That cadmium and selenium have toxic properties was first realised after these metals had already achieved commercial success.

What significance do heavy toxic metals have today in the cement industry? Since the mid 1980's strict regulations for gaseous emissions and immissions have started to be implemented in highly developed countries. In Europe, especially in Switzerland and Germany, very low limits have been set for the emission of various elements such as defined in the Swiss (LRV) and German (TA-Luft) Clean Air Acts. These regulations, given in Table 1, classify the toxic elements, mainly heavy metals, into various classes depending on their toxicity.

**Table 1:** The Limits for the Emission of Heavy Toxic Metals as Defined in the German (TA-Luft) and Swiss (LRV) Clean Air Acts

Element	Class	Class Emission Limits (mg/Nm <sup>3</sup> )
Cd	1	
Hg	1	0.2
Tl	1	
As	2	
Co	2	
Ni	2	1
Se	2	
Te	2	
Cr	3	
Cu	3	
Pb	3	
Pd	3	
Pt	3	5
Rh	3	
Sb	3	
Sn	3	
V	3	
Zn	n.c.	n. defined

Due to the very low emission limit of 0.2 mg/Nm<sup>3</sup> for the sum of the Class 1 elements (cadmium, mercury and thallium) and the high volatility of the elements mercury and thallium, Class 1 is of utmost importance to the cement industry. That thallium can be emitted from a cement plant is well documented (Figure 3) following the "incident" in 1979 at Dyckerhoff's Lengerich plant in which flora and fauna around the plant were shown to have suffered as a result of its emission. The source of this thallium was mainly the iron corrective used (4.8 ppm) and also the coal (1.2 - 1.8 ppm), both natural materials.

With the now common and ever increasing use of secondary materials, combustible and non-combustible, increased quantities of the heavy, toxic elements just defined are now being introduced into cement kilns. Which of these elements are the most common ones encountered, where do they come from and how do they behave inside the kiln? What happens to them after the cement is hydrated?

## **2. ESSENTIAL AND TOXIC ELEMENTS**

Whereas some elements are essential, others are decidedly toxic. Which elements fit into each category?

### **2.1 Essential Elements**

Those elements considered to be essential are given in Table 2.

**Table 2: Essential and Toxic Elements (Iyengar and Sansoni, 1976)**

**Structural Elements:** C, Ca, H, N, O, P, S

**Electrolyte Elements:** Ca, Cl, K, Mg, Na

#### **Trace Elements:**

- ◆ Essential
  - biologically important: Co, Cr, Cu, F, Fe, I, Mg, Mn, Mo, Ni, Se, Si, Sn, V, Zn
  - Clinically significant: Co, Cr, Cu, Fe, Mg, Se, Zn
- ◆ Suspected to be Essential: As, Ge, Rb
- ◆ Regularly Found in Tissue: Al, B, Br, Ga, Li, Sc, Sr, Ti
- ◆ Toxic
  - potentially toxic: As, Cd, Hg, Pb, Sb, Se
  - environmental contaminants: Cd, Hg, Pb
  - industrial hazards: Be, Bi, Cr, Mn, Ni, Sb, Th, Te, U, V, W

**Others:** Ag, Au, Ba, Ce, Cs, Nb, Pt, rare earths, Te, W, Zr

**Radioactive Contaminants:** Po, Ra, Rn, Th, U, Am, Cm, Np

Not all elements are toxic, indeed many are even essential to life. As can be seen in Table 2, the elements H, C, N, O, Na, Mg, P, S, Cl, Ca are the major elements necessary, the additional elements B, F, Si, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, Sn and I being necessary in only trace quantities. The main body of the essential trace elements is grouped between V and Zn in the first transition series of the periodic table. With the exception of Mo, Sn and I, all the essential elements lie within the first four layers of the table. The form in which these elements is present is also important as some compounds, eg. HCN (prussic acid) contain essential elements but must definitely be classed as being highly toxic.

Regarding the quantity of the trace elements required this varies from element to element. As given in Table 3, showing the situation for a 70 kg adult, the daily requirements range from 0.03 mg for Co up to 15 mg for Fe. These elements are not accumulated within the body and are excreted and so must be continually replaced. The total burden of the essential elements is also shown in Table 3 with Fe at 4.1 g (4100 mg) and Zn at 2.3 g (2300 mg) being the most abundant.

**Table 3: Estimated Daily Intake and Human Body Burden of Essential Trace Elements**

Element	Class*	Daily Intake (mg)	Burden (mg/70 kg)
Co	2	0.03	1
Ni	2	0.45	10
Se	2	0.06	15
Cr	3	0.06	6
Cu	3	3.2	100
V	3	2.5	30
Fe	n.c.	15	4,100
Mn	n.c.	5	20
Mo	n.c.	0.35	9
Zn	n.c.	12	3,200

\* Class in German and Swiss Clean Air Acts

## **2.2 Toxic Elements**

### **2.2.1 Toxicity**

Some of the substances which are emitted to the atmosphere during the burning of cement clinker are annoying and some can be even harmful to the environment. Annoying substances are those which only affect well-being, whereas harmful substances impair the biological activity (metabolism, growth) of an organism. In medical terminology the latter are referred to as "atoxic". While it is usual to speak globally of toxic elements, toxicity itself is by no means a fixed, well-defined property. Firstly it depends to a decisive extent on the chemical compound in which the particular element is found. For instance sulphur is very toxic as dioxide, hydrogen sulphide etc., but many other sulphur compounds are perfectly harmless e.g. sulphates like gypsum. It is also very important whether a compound is easily resorbed by the organism or not. Examples of compounds containing well-known "toxic" elements which on account of their being insoluble cannot be resorbed and are therefore practically harmless are:

- ◆ arsenic sulphide
- ◆ barium sulphate
- ◆ mercury sulphide

The tolerance limits for toxic elements to be found in official regulations are of course determined on the basis of the most dangerous compounds of the element concerned.

The toxic efficacy of a substance also depends to a large degree on whether it is absorbed by inhalation, ingestion or skin exposure. For example, metallic mercury can pass through the stomach and intestines without serious effects whereas inhaling the vapour can be very harmful. The toxicity of mercury compounds also depends on their solubility which in turn determines their absorption and distribution in the organism involved. Thus whilst metallic mercury and almost all mercury compounds are toxic, mercury sulphide is non-toxic because of its practical insolubility in the body.



Furthermore, a substance which harms one particular kind of organism can leave others entirely unaffected or even promote their biological activity. Moreover, the biological effect depends largely on the dose, as already recognized by the Swiss born physician and alchemist Paracelsus (1493 - 1541) who established the role of chemistry in medicine:

*"the dose alone decides whether a substance is poisonous or not"*

*"if given in small doses what makes a man ill also cures him"*

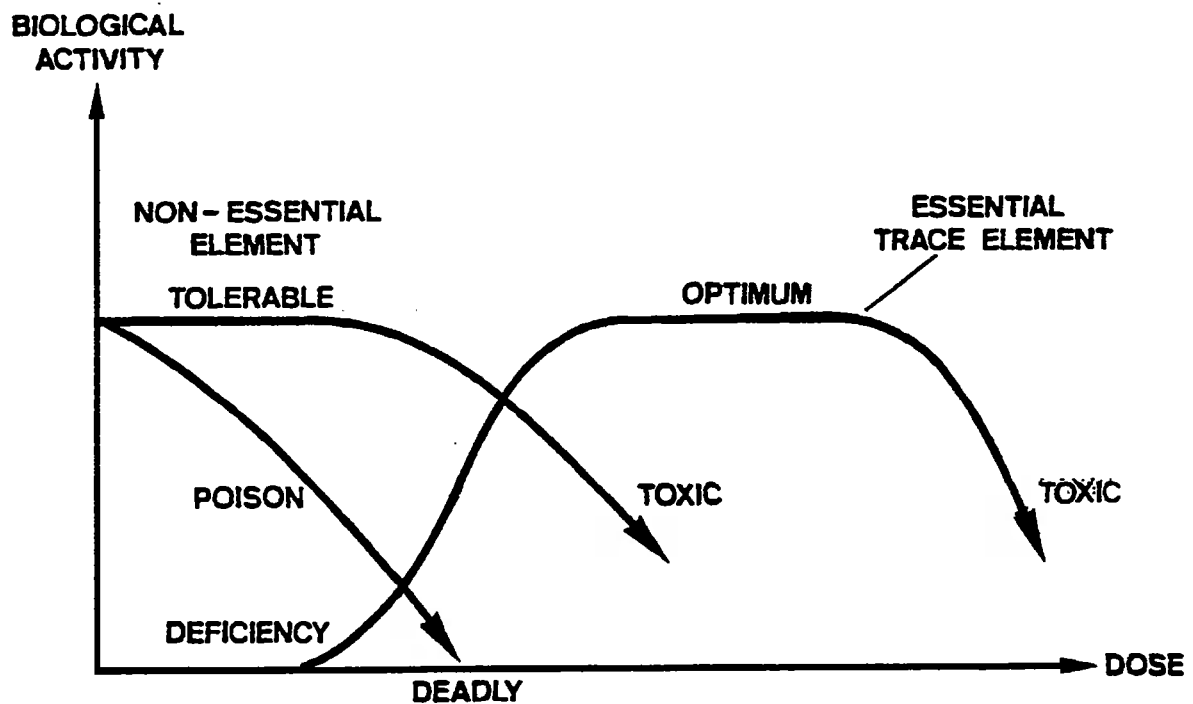
*"miners disease results from inhaling metal vapours and is not a punishment for sin administered by mountain spirits"*

No substance is absolutely harmless as there is always an upper limit to the concentration which may not be exceeded without serious consequences for the organism. For example, common salt is a dangerous poison when consumed in too large quantities. On the other hand, there is no absolutely toxic substance because below a certain minimum concentration even the strongest poison becomes ineffective.

Figure 1 shows schematically the basic relationship between dose and effect. In order to assess the toxicity of a substance, all the above factors have to be taken into account.

**Figure 1: Toxicity is a Question of the Dose**

Toxic Elements



In many cases it has been found that elements which are essential to life can also be toxic depending on the dose and the form in which the element is present. In general it can be said that the toxicity of elements roughly parallels their abundance in the Earth's crust and in sea water. Elements that are present in low levels are more likely to be toxic as shown in Table 4 in which those metals for which toxic properties have been reported are given. In this table mainly the toxic metals are included, the toxic non-metals having being omitted.

**Table 4: Composition of the Lithosphere indicating Essential and Toxic Elements**

Concentration (%)	Element
46.6	<b>O</b>
27.7	<b>Si</b>
8.1	<b>Al</b>
5.0	<b>Fe</b>
3.6	<b>Ca</b>
2.8	<b>Na</b>
2.6	<b>K</b>
2.1	<b>Mg</b>
$10^{-1}$	<i>Ti, H, Mn, P</i>
$10^{-2}$	<b>F, S, C, Cl, Rb, Sr, Ba, Zr, Cr, V, Zn</b>
$10^{-3}$	<b>Ni, Cu, Li, N, Sn, Co, Pb, Th</b>
$10^{-4}$ (ppm)	<i>As, B, Mo, Br, W, U</i>
$10^{-5}$	<i>Sb, Bi, Ag</i>
$10^{-6}$	<i>Hg, Se</i>
$10^{-7}$ (ppb)	<i>Au, Pt, He</i>
$10^{-8}$	<b>I</b>

essential elements in **bold text**, toxic elements in italics

Also presented in Table 4 are those elements previously shown in Table 3 which are essential for life. As can be seen many of the elements reported are considered as being both essential and toxic. Included in this category are the elements B, Mg, V, Cr, Mn, Co, Ni, Cu, Zn, Se, Mo and Sn. When, for example, a manganese deficiency occurs in humans this can be accompanied by anaemia, and bone changes in children. Considering the toxic effects of manganese these are listed as including metal fume fever, psychological and neurological disorders, the two latter being contracted after long term exposure to air containing freshly drilled dust particles rich in manganese ore. When a deficiency of copper occurs this is accompanied by a severe anaemia. Metallic copper is much less toxic than its salts and for humans only 1 g of  $\text{CuSO}_4$  is highly toxic, causing vomiting, diarrhoea, convulsions and is often fatal.

### **3. ANALYSIS OF TOXIC METALS**

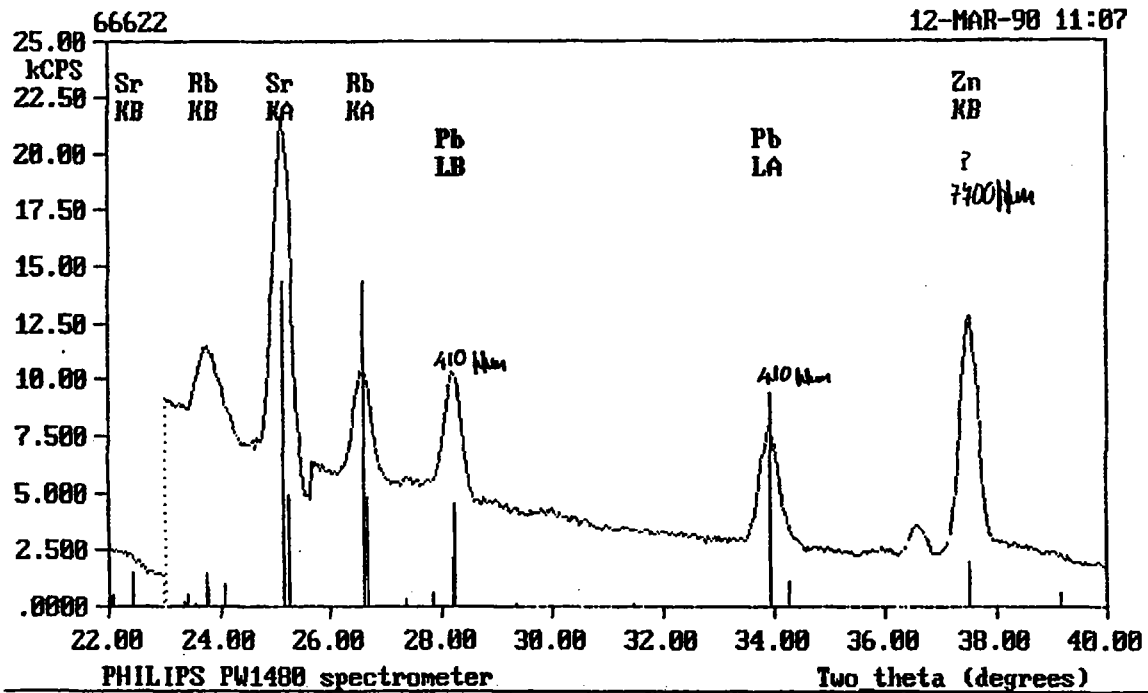
In order for a cement plant to be able to safely use secondary materials containing toxic metals without the risk of excessive emissions, it is essential that the materials received conform to the reference samples initially submitted. To do this it is necessary to carry out control analyses for those elements listed in the applicable Clean Air Act. This is especially the case, because of their volatility, for the Class 1 elements Hg, Tl and Cd but also for the elements of Classes 2 and 3 should these be present in appreciable concentrations. To avoid the necessity of carrying out a full quantitative analysis, which would be costly and time consuming and would attempt to determine elements even when they were not present, it is advisable to first carry out a qualitative analysis. This is the method used at HMC/TC.

#### **3.1 Qualitative Analysis of Toxic Elements**

A qualitative analysis (spectrum) of all the toxic elements with the exception of Be can be carried out using such methods as X-ray fluorescence (XRF) and inductively coupled plasma emission (I.C.P.) spectroscopy, provided that the instrument is of the sequential and not of the multi-channel type. Whereas the I.C.P. method requires the sample being measured to be in liquid form, both solid and liquid samples can be measured by the XRF, the latter being possible when the spectrometer is flushed with helium instead of operating under vacuum. Because of the comfort of the operating software and the general ease of operations the XRF technique is preferred at HMC/TC.

An example of an XRF spectrum is given in Fig. 2. This was taken using a sample of slightly contaminated excavated material being considered for disposal by incineration in a Swiss cement kiln. In this diagramme the wave length of the characteristic radiation (expressed as two theta in degrees for the measuring crystal) is presented on the x-axis and the intensity of the radiation (expressed as counts/sec) on the y-axis. As can be seen the presence of Pb (410 ppm) and Zn (7700 ppm) can easily be determined in this figure. The peak heights observed are not the same for equal concentrations of different elements. The peak height for different elements is not proportional to the quantity present. The values for these elements were found in subsequent quantitative determinations. Attempts to ascertain the qualitative presence of Cd, Hg and Tl, which were later shown to be present in quantities of 4.4, 0.14 and < 1 ppm, were not successful by this technique and should in any case always be quantitatively determined.

Figure 2: XRF Spectrum of excataed material



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### 3.2 Quantitative Analysis of Toxic Metals

Several methods can be used for the quantitative analysis of toxic metals and include those shown in Table 5. Of these the most sensitive of the methods that can generally be used is certainly the AAS technique with a graphite furnace which allows a lower limit of detection than the flame AAS, XRF and ICP methods. The limits of detection of the cold vapour and hydride AAS techniques lie within those of the two groups of methods previously mentioned. With regard to the limits of measurement these are some 4 to 5 times higher than the limits of detection.

**Table 5: Detection Limits (ppm) of Environmentally Sensitive Elements by Various Measurement Techniques**

Element	Class	AAS Flame	AAS Furnace	AAS Cold Vapour	AAS Hybride	ICP	XRF
Be	1 Car.	1	0.003			0.003	
Cd	1	1	0.0002			1.5	1 - 10
Hg	1	200		0.1	0.05	12	
Tl	1	30	0.01			27	
As	2	100	0.08		1	30	
Co	2	5	0.008			3	
Ni	2	8	0.05			4	1 - 10
Se	2	100	0.05		1	30	
Te	2	70	0.03		0.50	20	
Cr	3	3	0.04			3	
Cu	3	2	0.005			1	
Pb	3	20	0.007			25	
Pd	3	20	0.05			13	1 - 10
Pt	3	50	0.20				
Rh	3	2	0.01			8	
Sb	3	60	0.08		5	40	
Sn	3	80	0.03		5	30	
V	3	20	0.10			3	
Zn	n.c.	0.6	0.003			2	1 - 10

In HMC/TC laboratories, where all the above methods are available Hg is measured by the hydride process and all the others with a few exceptions using the graphite furnace AAS technique. These methods were chosen because, being wet chemical techniques, there is no matrix correction and standard calibration samples are easily made by the addition method.

### 3.3 Evaporation of Mercury during Handling in Laboratory

It should be pointed out that sampling and sample preparation are most important aspects of a trace element analysis. Contamination or the loss of a portion of an element are an omnipresent danger. This is actually the reason why there are often doubts about the validity of values given in literature, particularly at low concentration levels. An evaporation test demonstrated that varying amounts of mercury can escape during the preparation and drying of a sample (see Table 6).

**Table 6: Hg-Concentrations in Precipitator Dust and Sewage Sludge Samples after Treatment at Different Temperatures**

Temperature (°C)	ESP Dust (ppb)	Sewage Sludge (ppb)
20	430	6,400
100	90	6,400
200	60	6,300
300	40	700

## 4. SOURCES OF TOXIC METALLIC SUBSTANCES

### 4.1 Common Sources of Toxic Metallic Substances

To provide an overview with regard to the normal uses to which the elements of Classes 1, 2 and 3 of the previously mentioned Clean Air Acts are put, Appendix II gathers together some relevant information. As can be seen all of the elements are extracted from ores in which they are present as either oxides or sulphides and are thus found in nature in water insoluble forms. In nature they are often only present in low concentrations but after extraction are then present in much higher concentrations and may be in a soluble form. The information given in Appendix II is intended to inform the reader which industries are likely to have by-products that could contain the listed elements. Although it is very unlikely that any of the primary products listed in the "uses" table would ever be considered as secondary materials the same cannot be said for the by-products of these manufacturing industries, which because of restrictions on dumping materials, are now looking for other means of disposal. Today some Group plants are in fact disposing of preservatives, pigments, dyes etc. which enter the kiln via secondary materials such as waste oils or woods.

### 4.2 Natural Cement Raw Materials Components

As shown earlier in Table 4 the heavy toxic metallic elements make up a small but definite proportion of the materials in the Earth's crust. As such their introduction into a cement kiln via the natural raw materials cannot be prevented. This question of interest is therefore how much of the classified and non-classified elements (at the ppm and ppb levels) can be present in the various rock types used for raw mix components?

The answer to the above question is given in Table 7 for the main rock types limestone, limey marl and clays and in Table 8 for the commonly used corrective, iron ore. As can be seen in Table 7 the limestone and limey marl components tend to have lower contents of heavy metals than clay components. This does not mean, however, that all limestones can be assumed to be low in heavy metals. In fact Zn levels of 1900 ppm and V levels of 3000 ppm have been encountered in extreme cases.

For the limey marls reported the values were all low and in the same magnitude or lower than the average levels in the Earth's crust. The highest level was 55 ppm reported for Zn.

When considering the heavy metals present in iron ore, an often used corrective, as shown in Table 8 such materials can often contain concentrations of heavy metals appreciably higher than the average for the crust. Such elements include Ti (400 ppm), As (680 ppm), Cr (1500 ppm), Pb (8700 ppm) and Zn (9400 ppm). It is fortunate that only small quantities of iron corrective have to be used in cement kiln raw mixes.

In the case of the clays values very much higher than in the Earth's crust were reported for Cd (500 ppm), Cr (1500 ppm), V (3600 ppm) and Zn (1300 ppm).

**Table 7: Range (ppm) of Heavy Metals Reported for Rock Types Used as Raw Mix Components**

Element	Class	Limestone	Limey Marl	Clay	Earth's Crust
Cd	1	0.02 - 0.50	0.04 - 0.35	0.02 - 500	0.2
Hg	1	0.005 - 0.10	0.009 - 0.13 0.02 - 0.15	0.08	
Tl	1	0.05 - 1.8	0.07 - 0.68	0.20 - 1.6	0.5
As	2	0.1 - 12		3 - 25	1.8
Co	2				25
Ni	2	1.4 - 13	5.9 - 21	11 - 71	75
Se	2				0.05
Te	2				0.01
Cr	3	0.70 - 16	4.6 - 35	20 - 1500	100
Cu	3				55
Pb	3	0.27 - 21	1.3 - 8.5	1.0 - 219	13
Sb	3				0.2
Sn	3				2
V	3	5 - 3000		30 - 3600	135
Zn	n.c.	0.10 - 1900	24 - 55	2 - 1300	70

**Table 8: Range (ppm) of Heavy Metals Reported for Correctives used in Cement raw Mixes**

Element	Class	Iron Ore	Earth's Crust
Cd	1	0.2 - 15	0.2
Hg	1		0.08
Tl	1	0.07 - 400	0.5
As	2	4 - 680	1.8
Co	2		25
Ni	2	10 - 340	75
Se	2		0.05
Te	2		0.01
Cr	3	9 - 1400	100
Cu	3		55
Pb	3	9 - 8700	13
Sb	3		0.2
Sn	3		2
V	3		135
Zn	n.c.	6900 - 9400	70



### 4.3 Secondary Raw Meal Components

To improve the economics of clinker production or improve cement quality many plants are today using so called secondary components in their raw mixes. These materials are mainly waste products from other processes and are often available in large quantities. Examples of such materials are given in Table 9 with fly ash and foundry sand in a few cases being the main alumino-siliceous raw mix component. Of these the purest material is probably the man made FCC catalyst but, depending on the source of the oil being processed in the refinery, this material can contain up to 1860 ppm of Ni, 1265 ppm of Sb and over 5000 ppm of V. As can be seen a natural material such as fly ash can contain up to 530 ppm of As, 600 ppm of Ni, 650 ppm of Cu, 800 ppm of Pb, 500 ppm of V and 910 ppm of Zn. In cases in which coal is used as the main fuel and fly ash as a major mix component, appreciably levels of heavy metals may be introduced into the kiln. Foundry sand is a component that is just starting to be used but as seen in Table 9 may contain appreciable maximum levels of Ni (1520 ppm), Cu (1500 ppm) and Pb (2300 ppm).

**Table 9: Range of Heavy Metals (ppm) in Secondary Components used in Cement Raw Mixes**

Element	Class	Foundry Sand	FCC Catalyst	Fly Ash	Earth's Crust
Cd	1	300	< 0.6	0.2 - 8	0.2
Hg	1	2	0.04 - 2	0.2 - 0.8	0.08
Tl	1		< 1.5 - 145	2 - 15	0.5
As	2	2	2 - 6	40 - 530	1.8
Co	2		13 - 93	90 - 250	25
Ni	2	1,520	265 - 1860	150 - 600	75
Se	2	1	< 11 - 128	1 - 35	0.05
Te	2				0.01
Cr	3	10	58 - 142	60 - 330	100
Cu	3	1,500	6 - 93	140 - 650	55
Pb	3	2,300	12 - 174	125 - 800	13
Sb	3		<25 - 1265	0.5 - 90	0.2
Sn	3	100	7 - 23	(38)	2
V	3	5	1050 - 5515	230 - 500	135
Zn	n.c.	130	32 - 115	350 - 910	70

#### 4.4 Toxic Elements in Raw Meal

The levels of the heavy toxic elements previously given for the mix components, major, minor and secondary give the maximum range encountered on a world-wide basis. Of more importance is the levels of the classified elements that are actually encountered in practice and these are presented in Table 10. As can be seen the concentrations of many elements are less than the average for the crust. The only elements which are present in concentrations above the average for the Earth's crust are limited to Tl (6 ppm) and As (28 ppm). These levels can in no way be considered as high.

**Table 10: Heavy Toxic Metal Levels (ppm) in Raw Meal**

Element	Class	Raw Meal	Earth's Crust
Cd	1	0.04 - 1	0.2
Hg	1	< 0.02 - 0.6	0.08
Tl	1	0.1 - 6	0.5
As	2	3 - 28	1.8
Co	2	11	25
Ni	2	18 - 30	75
Se	2	< 0.2	0.05
Te	2		0.01
Cr	3	23 - 39	100
Cu	3	17	55
Pb	3	4 - 15	13
Sb	3		0.2
Sn	3		2
V	3	32 - 102	135
Zn	n.c.	15 - 90	70

#### 4.5 Natural Fuels

Because the normally used fuels coal and oil have been formed over millions of years by naturally occurring processes in the Earth's crust, it will not now be surprising that these also contain heavy, toxic elements in trace quantities. The quantities reported by various authors are given in Table 11.

As can be seen brown coal contains the smallest quantities of classified heavy metals with only Zn at up to 70 ppm being above the 10 ppm level. For hard coal the maximum quantities of the major heavy metals present are Pb (270 ppm), Zn (220 ppm), V (180 ppm), Ni (96 ppm) and Cr (80 ppm). For bunker oil the heavy metals present in the maximum concentrations are V (117 ppm), Zn (85 ppm) and Ni (43 ppm). For petcoke, a residue of oil distillation, the levels of the heavy metals are more concentrated with the maximum levels reported being Ni (355 ppm) and Cr and Pb at both just over 100 ppm.

**Table 11: Range of Heavy Metals (ppm ) in Natural Fuels Used in Clinker Production**

Element	Class	Hard Coal	Brown Coal	Petroleum Coke	Bunker Oil	Hard Coal Fly Ash	Earth's Crust
Cd	1	0.1 - 10	0.1 - 2.4	0.1 - 4.0	0.02 - 0.4	0.2 - 8	0.2
Hg	1	0.1 - 1.0		0.01 - 0.09		0.2 - 0.8	0.08
Tl	1	0.1 - 1.2	0.07 - 0.3	0.04 - 3.1	< 0.02 - 0.12	2 - 15	0.5
As	2	2 - 50	0.3 - 9		< 0.01 - 0.1	40 - 530	1.8
Co	2	5 - 34				90 - 250	25
Ni	2	15 - 96	0.6 - 1.9	24 - 355	5 - 43	150 - 600	75
Se	2	0.6 - 3.4				1 - 35	0.05
Te	2	0.2 - 0.6					0.01
Cr	3	5 - 80	0.9 - 8	3.6 - 104	2 - 4	60 - 330	100
Cu	3	10 - 60				140 - 650	55
Pb	3	10 - 270	0.8 - 6	6 - 102	1 - 34	125 - 800	13
Sb	3	0.4 - 2.0				0.5 - 90	0.2
Sn	3					(38)	2
V	3	30 - 180	2 - 7		2 - 117	230 - 500	135
Zn	n.c.	6 - 220	1 - 70	(7.6)	5 - 85	350 - 910	70

#### 4.6 Secondary Fuels

Table 12 lists the range of heavy metals used in the most commonly used secondary fuels. As can be seen, the levels of many elements are below the average for the Earth's crust but, when these latter values are exceeded, this is by a considerable margin and in elements specific for the individual fuel concerned.

For example waste automobile oil is enriched in those elements which are introduced by the wear of bearing materials. Thus elevated values of Pb (21'000 ppm) and Zn (3000 ppm) are to be found in waste oil. Automobile tyres are especially enriched in Zn for which levels between 0.93 % and 2.05 % are reported. The impurities in used ion exchange resins will depend on the material stream which they have been used to clean up, with especially high levels being reported for Pb (6400 ppm) and Zn (3900 ppm). In contrast the levels of the heavy metals in used wood are considerably lower but with maximum values of Cd (16 ppm), Se (5ppm), Cu (77 ppm), Pb (70 ppm), Sb (10 ppm) and Zn (560 ppm) which are definitely above the average level in the crust.

**Table 12: Range of Heavy Metals (ppm ) in Secondary Fuels Used in Clinker Production**

Element	Class	Waste Oil	Fullers Earth	Ion Exchange Resins	Automobile Tyres	Used Wood	Earth's Crust
Cd	1	4	0.01 - 2	9 - 50	5 - 10	1.5 - 16	0.2
Hg	1					< 0.05	0.08
Tl	1	0.02	0.2	0.03 - 0.07	0.2 - 0.3	0.5	
As	2						1.8
Co	2						25
Ni	2	3 - 30	0.001 - 30	8 - 87	77	11 - 50	75
Se	2					5	0.05
Te	2						0.01
Cr	3	5 - 50	2 - 11	20 - 330	97	16 - 25	100
Cu	3					40 - 77	55
Pb	3	10 - 21000	2 - 2500	150 - 6400	60 - 760	38 - 70	13
Sb	3					10	0.2
Sn	3						2
V	3						135
Zn	n.c.	240 - 3000	10 - 480	56 - 3900	9300 - 20500	130 - 560	70

## 5. BEHAVIOUR OF TOXIC METALS IN CEMENT KILNS

Now that we know the concentrations of the heavy toxic metals in the raw material components and fuels let us now turn our attention to the behaviour of these metals in the cement kiln.

### 5.1 Volatility of Toxic Element Compounds

To gain an impression of the volatility behaviour of the toxic metals listed in the German and Swiss Clean Air Acts, the vapour pressures of the most likely compounds to be present in a cement kiln, i.e. when the elements are not incorporated into the lattice of the clinker minerals, have been reviewed by Haegermann. Those having a partial pressure of at least 1 mm Hg at 300°C are listed in Table 13. As can be seen in addition to the high volatility of Hg compounds, which are essentially completely emitted from cement kilns, other elements listed in the German clean air act (Be, As, Se and V) can all form compounds with vapour pressures of 1 mm Hg at temperatures of lower than 300°C and are hence capable of being emitted from cement kilns.

**Table 13:** Heavy Metal Compounds of Class 1, 2 and 3 Elements which have a Partial Pressure of over 1 mm Hg at or below 300 °C

Element	Class	Fluoride	Chloride	Bromide	Iodide	Oxide	Sulphate	Hydride	Meta l
Be	1 carcin		*	*	*				
Cd	1								
Hg	1		*	*	*				*
Tl	1								
As	2	*	*	*	*	*		*	
Co	2								
Ni	2								
Se	2	*	*			*			
Te	2								
Cr	3								
Cu	3								
Pb	3								
Sb	3								
Sn	3								
V	3								

## **5.2 Distribution of Toxic Heavy Elements**

For a comprehensive assessment of the distribution volatilization and emission of an element, the exact balance of its intake and output must be known. To this end it is necessary to analyse all material and gas streams, such as raw mix and fuel, in order to determine the intake and the amount present in clinker and discarded dust.

Normally these calculations of the balances indicate that the total intake of an element from raw material ( $I_r$ ) and from fuel ( $I_f$ ) minus discharges via clinker ( $D_c$ ) and discarded dust ( $D_d$ ) equals the emission ( $Ex$ ) plus that portion ( $R_k$ ) retained inside the kiln system:

$$I_r + I_f - D_c - D_d = Ex + R_k \quad (1)$$

According to the behaviour of the elements in cement kilns, three separate cases can be distinguished, one for non-volatile and two for volatile compounds:

- ♦ Case 1: For non-volatile compounds:  $I_r + I_f = D_c$ , i.e. there is no emission and no accumulation in the kiln system:  $Ex, R_k = 0$
- ♦ Case 2: For volatile compounds:  $I_r + I_f > D_c$ 
  - (a): surplus intake remains totally in the "kiln" system with no emission, i.e.  $Ex = 0$
  - (b): surplus intake is wholly emitted with no retention in the kiln:  $R_k = 0$

The transposition of equation (1) results in:

$$D_d + R_k = I_r + I_f - D_c - Ex \quad (2)$$

To a first approximation the terms on the right side of the equation (2) can be considered as constant:

$$D_d + R_k = \text{constant} \quad (3)$$

By means of equation (2) it is possible to calculate that a certain portion of a compound will remain in the kiln system if no dust is rejected and also the amount of dust required to be rejected in order to keep the retained portion  $R_k$  below a certain limit. For this purpose it is necessary to know the emission  $Ex$ . Only limited data are available for the latter as this is sensitive information which cement plants do not make readily available.

The quantity emitted  $Ex$  can, however, be estimated if it is known which of the three cases best describes the compound in question.

According to HMC/TC's own investigations and the findings of the Research Institute of the German Cement Industry (VDZ), the Class 2 and 3 elements are not likely to exceed the emission limits of 1 resp. 5 mg/Nm<sup>3</sup>, respectively, in normal operation and with normal raw materials. Even if sewage sludge is used as combustible, as partial substitute for coal, the emission of all Class 2 and 3 elements is well below the limits. The elements of Class 1, especially Hg and Tl show quite a different behaviour. This Class, characterized by its very low emission limit of 0.2 mg/Nm<sup>3</sup>, represents a permanent danger, a fact which also becomes evident from the concentration of the elements in the Earth's crust shown in Tables 7 to 12. Therefore, it is worthwhile to give a more detailed description of the findings of these investigations.

### **5.3 Distribution of Cadmium**

According to HMC/TC's measurements, the degree of binding of cadmium in clinker shows very large variations from 41 to 100 %. This corresponds to the findings of Sprung (VDZ). The reasons for the variations are not clear. Relatively small temperature fluctuations and also the burning conditions will have an effect. Due to the fact that the clinker absorbs only part of the cadmium and the emission is insignificant, the rest will remain in the kiln system causing recirculations with cadmium enrichment in different materials. The cadmium concentration increases from raw meal to electrostatic precipitator dust to the hot meal. The dust shows large differences in concentration between direct and compound operation. These findings show that cadmium as a partly volatile element belongs to case 2(a) with no emission ( $Ex = 0$ ) but with accumulation in the kiln system.

### **5.4 Distribution of Mercury**

The investigation of different materials has shown that the mercury contents vary widely and are relatively low in raw materials and coal compared to the average concentration in the lithosphere.

Mercury was not detected in clinker, however, in some cases an accumulation was observed in kiln dust, although these concentrations (max. 190 mg/t) are insignificant compared to the other elements, e.g. thallium. Furthermore, it should be mentioned that the mercury emission in compound operation is appreciably lower than that in the direct mode. In compound operation the emitted quantities are even lower than the intake. Obviously, much of the mercury vapour is retained in the raw mill perhaps by adsorption on the surface of the meal particles. In direct operation, the retained mercury will be released again and is emitted.

Summarising, it can be generally stated that the mercury introduced by raw materials and fuels is completely emitted in gaseous form (in the dry process mainly in direct operation) so that its behaviour is that of a volatile compound without retention in the kiln ( $R_k = 0$ , i.e. case 2b). These findings were also confirmed by the stack gas analyses available.

### **5.5 Distribution of Thallium**

According to German investigations (Sprung, VDZ) and HMC/TC findings, cement raw mixes contain about 100 to 800 mg thallium per ton corresponding to 150 to 1200 mg thallium per t clinker. The concentration can be much higher in kiln feed and coal dust because large quantities of thallium are accumulated from the kiln gases during drying and grinding. Furthermore, the kiln feed shows significant differences between direct and compound operation: The thallium concentration increases considerably during direct operation and may ultimately be up to 8 times as high as in the compound mode. The measurements reveal that neither the clinker nor the stack gas discharge the kiln system of thallium. Only very high exhaust gas temperatures above 200°C (long dry and wet kilns) may allow some thallium vapour to escape. Nearly the entire intake remains in the system. Therefore, thallium is to be considered as a volatile compound with no emission ( $Ex = 0$ ) and no output by the clinker ( $Ac = 0$ ), i.e. all TI is accumulated in the kiln system. Hence, as will be appreciated in light of the "Lengerich incident" it is particularly important to relieve the kiln/grinding system e.g. by creating a "valve" in order to avoid excessive accumulations of thallium which ultimately lead to kiln dust with extremely high TI concentrations. Especially in cases of disturbed operations e.g. insufficient or lacking precipitator function could the emission of TI become considerable.

## 5.6 Typical Balance of Toxic Elements In Kilns

### 5.6.1 Wet Kiln

A simple balance of the toxic elements in a large wet kiln fired with coal is displayed in Table 14 in which the percentage input as coal and slurry as well as the output via the clinker, dust and stack gas are given. Here a simplified case is presented in that the totals for the inputs and outputs are all 100 %. As can be seen the major input always comes from the slurry but for As and Be almost 25 % is delivered from the coal. At the other end of the scale less than 10 % of the elements Pb, Tl and Zn comes from the fuel.

**Table 14: Balance (% total) of Toxic Elements in a Large Wet Kiln**

Element	class	Input slurry	Input coal	Output clinker	Output E.S.P.dust	Output Stack
Be	1 carcin	76	24	96	4	0
Cd	1	82	18	18	81	1
Tl	1	95	5	22	14	42
Ni	2	82	18	97	3	0
As	3	77	23	92	8	0
Pb	3	93	7	22	77	1
Zn	n.c.	93	7	88	12	0

Regarding the output of Hg, although not mentioned, this essentially leaves the kiln system completely via the stack gas. The next most volatile element was found to be Tl of which 42 % of the total input left the kiln in the stack gas whilst for Cd and Pb only 1 % left by this way.

Of the elements which did not leave the kiln system, with the exception of Tl these were mainly found in either the filter dust or in the clinker. Those less volatile elements found predominantly in the clinker were As (92 %), Be (96 %), Ni (97 %) and Zn (88 %). In contrast, for the more volatile species, 81 % of the Cd and 77 % of the Pb were found in the kiln dust.

### 5.6.2 Lepol Kiln

An example from Krcmar et.al. of a heavy metal balance for a Lepol kiln fired with petroleum coke as fuel is presented in Table 15. This presentation is more comprehensive than that previously given in that the actual concentrations of the individual elements are given for the various types of inputs and outputs. Those elements leaving the kiln in the form of a vapour were not measured and the fact that the output can be either higher or lower than the input is acknowledged, these indicating a gain resp. loss within the kiln system. A missing output therefore does not automatically mean the emission of the element concerned as a vapour. This is certainly the case for Tl where additional measurements showed that the missing Tl was not being emitted.



On the basis of the present balance the volatility of the classified heavy elements can be classified by the volatility factor  $f$ , defined as:

$$f = \text{concentration in clinker} / \text{concentration in raw meal}$$

The following classes have been defined

- ♦ volatile ( $f = 0$  to  $0.35$ ): Cd, Tl, Se, Pb
- ♦ semi-volatile ( $f = 0.7$  to  $1.1$ ):
- ♦ on-volatile ( $f = 1.2$  to  $2.7$ ): As, Co, Ni, Cr, Cu, Sb, Zn

**Table 15: Heavy Metal Balance for a Lepol Kiln Fired with Petroleum Coke (Concentrations marked \* given in ppb)**

**TOXIC ELEMENTS IN KILN DUST**

Element	Class	Input						Output							
		r.meal (ppm)	r.meal (%)	petcoke (ppm)	petcoke (%)	missing (ppm)	missing (%)	clinker (ppm)	clinker (%)	E.S.P. dust (ppm)	E.S.P. dust (%)	Stack (ppm)	Stack (%)	missing (ppm)	missing (%)
Cd	1	*367.8	98.80	*4.5	1.20			*783.9	22.50	*138.1	37.10	*8.2	2.20	*142.1	38.20
Tl	1	*557.4	99.20	*4.8	0.80			*53.3	9.30	*413.6	75.40	*29.1	5.10	*58.2	10.20
As	2	18.20	99.40	0.10	0.60			17.90	97.80	0.20	1.10	<<0.1	<0.1	0.20	1.10
Co	2	17.40	98.40	0.30	1.60			17.90	99.50	0.10	0.30	<<0.1	<0.1	0.10	0.20
Ni	2	32.10	56.00	25.20	44.00			53.20	92.80	2.60	4.50	0.10	0.20	1.40	2.40
Se	2	2.80	100.00							< 0.1	0.40	< 0.1	0.40	2.80	99.20
Te	2														
Cr	3	45.60	98.90	0.50	1.10	0.20	0.40	45.80	99.30	0.50	1.10	<0.1	<0.1	1.40	2.40
Cu	3	31.40	99.10	0.30	0.90	0.50	1.60	32.00	100.90	0.20	0.60	0.10	0.10		
Pb	3														
Pd	3														
Pt	3														
Rh	3														
Sb	3	1.40	95.20	<0.1	4.80	0.10	3.40	1.50	102.70	<0.1	0.70	<0.1	<0.1		
Sn	3	3.30	99.10	0.10	0.90			2.90	86.90	< 0.1	0.60	<< 0.1	0.10	0.40	12.50
V	3	76.70	47.50	84.90	52.50			135.80	84.00	18.40	11.40	0.90	0.60	6.50	4.00
Zn	n.c.	48.10	96.60	1.70	3.40	3.20	6.40	50.20	100.80	2.70	5.40	0.10	0.20		

The concentrations of toxic elements in cement kiln dusts have been measured for the wet, semi wet/semi dry and dry types of cement kiln and also for rotary lime kilns. The results obtained are listed in Table 16 in which it can be seen that no values are given for mercury (Hg) due to the fact that it is essentially wholly emitted and not retained in the dust or in the clinker. The values given refer to a period prior to the introduction of the German (TA Luft) and Swiss (LRV) Clean Air Acts. In some cases the plants were using secondary materials (combustible and non combustible) and also iron pyrites as a corrective. In those cases where the filter dust was sampled the values given in Table 16 are indicative of the range of these toxic elements and, as far as is known, are in no way associated with the burning conditions. It is not possible to adjust conditions to ensure that the toxic elements are steered into the clinker minerals and not into the dust. The values given for the stack gas dust are again indicative of the raw materials used but now for their interpretation the efficiency of the filter system must also be taken into consideration.

**Table 16: Concentration (in ppm) of Toxic Elements in Kiln Dusts**

Class	Kiln	Wet	Semi	Dry	Lime
1	Cd	1-21	3-120	1-15	1-2
1	Tl	1-237	43-586	1-617	1-56-69
2	As	63-225	1-103	37-222	12-33
2	Co	1-2	1-11	1-169	41-765
2	Ni	11-75	20-87	22-4145	61-90
3	Cr	37-65	61-282	31-4107	
3	Cu	45-1180	128	44-69	27-77
3	Pb	31-2830	522-7000	12-321	
3	V	77-79	12-321	1-33	
n.c.	Zn	80-4500	27-77	107-147	

### 5.7 Class 1 Elements (Cd and Tl)

As seen in Table 16 the values for these elements can be as low as 1 ppm to as high as 120 ppm in the case of Cd and 617 ppm (0.06 %) for Tl. It is interesting that both the wet and dry kiln dusts had all Cd values essentially under 20 ppm whereas for the semi processes the lowest value was 31 ppm and the highest 120 ppm. When Tl is considered, which is mainly to be found in the dust and not in the clinker, no obvious trend could be seen but again the lowest value for semi processes was higher than for the wet and dry types. For the two lime kiln dusts studied, for which limestone was the only component of the kiln charge, the levels of Cd and Tl were both under 2 ppm, an indication that the limestone is usually low in toxic metals.

### 5.8 Class 2 Elements (As, Co and Ni)

Of the five Class 2 elements only As, Co and Ni were determined as the elements Se and Te are not often encountered. The absence of these elements should not be taken for granted as they are in the same column of the periodic table as S, and their absence should be first be confirmed by taking an XRF-spectrum. In one secondary fuel tested at HMC/TC the level of Se was found to be 12'000 ppm i.e. 1.2 %.

For As the values found in the dusts ranged essentially from 37 to 225 ppm, for Co from 1 to 169 ppm, with all values except one being under 37 ppm, and for Ni from 11 up to 4145 ppm (0.41 %) in an extreme case. For Ni the values were either under 200 ppm or well above with the extreme values all being for dry process kilns. With regard to the lime kiln dusts the maximum values were 69 ppm for As, 33 ppm for Co and 765 ppm for Ni.

### 5.9 Class 3 Elements (Cr, Cu, Pb, V)

The very exotic elements in this class (Pd, Pt and Rh) as well as Mn, which is always present in cement raw materials in small percentages, were not analysed. Up to date none of the very expensive elements have ever been found in XRF-spectra performed at HMC/CS.

Regarding the toxic metal Cr, whose presence is associated with chrome eczema, this has been found in quantities between 31 and 4107 ppm (0.41 %) in kiln dusts. Most values lie under 300 ppm and the appreciably higher values were found in only three cases. With regard to Cu most values lie between 40 to 70 ppm and only in two cases (128 ppm and 1180 ppm) were higher values determined.

The toxic element present in the highest levels in kiln dust was found to be Pb which ranged in value between 12 and 7000 ppm (0.7 %). For this element the level in the dusts of the

semi process plants were definitely the highest and with only two exceptions the values lie between 1274 and 7000 ppm. For the dry process plants no values were higher than 321 ppm and for wet process kiln dusts most were lower than 150 ppm but with two extreme values of over 2220 ppm. The levels determined for V lie between 1 and 79 ppm and so are under the average level of this element (110 ppm) present in the Earth's crust.

#### **5.10 Non-Classified Elements**

Although Zn is not specified in the German and Swiss Clean Air Acts it can be found in kiln dusts. The levels found ranged mainly between 80 and 230 ppm with one extreme value of 4500 ppm (0.45 %) also being found. This highest value was determined on a stack gas dust.

#### **5.11 Maximum Allowed Levels in Stack Gas Dust**

Although the levels of the toxic elements present in the emitted stack gas dusts are high, their significance should be considered by taking not their concentrations but the quantities actually emitted into consideration. If it is considered that the maximum allowed emissions or Classes 1, 2 and 3 are 0.2, 1.0 and 5.0 mg/Nm<sup>3</sup> respectively, then for a stack gas stream with 50 mg/Nm<sup>3</sup> dust load the maximum allowed concentrations in the dust are 0.4 %, 2.0 % and 10.0 %. In none of the cases investigated did the emissions come near to these values and even with filters of poorer efficiency is it unlikely that the limits would be exceeded.

### **6. TOXIC ELEMENTS IN CLINKER**

#### **6.1 Levels of Toxic Elements**

The levels of toxic elements in clinkers, reported in the literature are given in Table 17. As can be seen for the elements of Class 1 i.e. Cd, Hg and Tl, the levels found were at the highest 1.5 ppm in the case of Cd. For the elements of Classes 2 and 3 the values reported, with the exception of Se, varied over a larger range. The lowest values could be low for As (2ppm), Pb (1 ppm) but could be much higher such as in the case of Zn (530 ppm), Ni (400 ppm) and Cr (320 ppm)

**Table 17: Range of Heavy Metals (ppm) in Clinker**

Element	Class	Clinker	Earth's Crust
Cd	1	0.01 -1.5	0.2
Hg	1	< 0.01 -0.12	0.08
Tl	1	<0.01 -1.2	5
As	2	2 -87	1.8
Co	2	10 -21	25
Ni	2	10 -397	75
Se	2	<0.2 -<1.0	0.05
Te	2		0.01
Cr	3	10 -319	100
Cu	3	5 -136	55
Pb	3	1 -105	13
Sb	3	0.1 -1.5	0.2
Sn	3	(2.9)	2
V	3	10 -135	135
Zn	n.c.	29 -531	70

## 6.2 Influence of Toxic Metals on Cement Properties

As just seen in Table 17 the highest concentration of a toxic element found in clinker was 531 ppm (0.05 %) in the case of Zn and 397 ppm (0.04 %) for Ni. What effect will these have on cement properties?

From the studies of C. Tashiro the influence of additions of Cr, Cu, Zn, Cd, Hg and Pb, in both soluble and poorly soluble forms has been well documented. At an addition level of 0.5 % on a clinker basis no appreciable changes in hardening properties were detected and thus with the much lower levels of these metals, and then already incorporated within the clinker, definitely no change in cement properties is expected. The results of studies in which toxic metal dosages to cement of appreciably more than 0.5 % and which showed retarding and accelerating properties are not relevant to the properties of clinker. Statistical studies by Blaine on normally produced cements also showed that at the levels of the toxic metals present in clinker no changes are to be expected.

## 6.3 Ability of Clinker Compounds to Immobilize Toxic Metals

At the present time much research is being carried out into the use of cements to immobilize the toxic metals present in ashes, slags and other industrial waste materials so that they are not removed by leaching after dumping in an approved site. From the studies of Bhatti it is known that the toxic elements can be incorporated into the structure of the CSH-gel during its formation but can also enter the structure after its formation with the displacement of Ca ions. In certain cases new unknown compounds containing a toxic metal may also be formed.

From the studies of the VDZ (Sprung) it is known that even the water soluble toxic elements will be completely immobilized on hydrating. This has been shown to be the case from studies in which larger quantities of toxic metals than are possible in clinker as found in wastes have been completely bonded by the use of cement pastes. The bonding is chemical and adsorptive together with the formation of a dense structure.

From the data shown in Table 18 it can be seen that the solubility of the toxic metals in a cement suspension is between  $10^{-1}$  and  $10^{-6}$  % of the quantities present.

**Table 19:** (1) Solubilities of Heavy metal Compounds at pH Values of 12.6 to 13.0:  
(2) Leaching Rates of Compacted Mortars (11 % Cement) after 28 Days Hardening

Element	Solubility in $\text{Ca(OH)}_2$ / KOH Solution	Solubility in Cement Suspension (%)	Degree of Solubility (%) from Mortar
As	$8 \times 10^{-3}$	$4 \times 10^{-5}$	
Pb	93	$7 \times 10^{-3}$	
Zn	$1 \times 10^{-4}$	$2 \times 10^{-6}$	
Cd	$1 \times 10^{-4}$	$< 1 \times 10^{-6}$	$2 \times 10^{-4}$
Tl	90	$1 \times 10^{-1}$	$1 \times 10^{-4}$

With regard to the leaching out of the elements from 28-day mortars prepared with 11 % by weight of cement, the quantity of the elements removed by the eluate was maximum  $2 \times 10^{-4}$  % of the quantity added. With regard to the small quantities normally present in clinker these will be certainly immobilized when the cement is present in hydrated form in concrete.

## 7. INFLUENCE OF KILN TYPE ON HEAVY METALS EMISSIONS

### 7.1 Experience from Literature and Plants

#### 7.1.1 Non-Volatile Metals

Emission of low or non-volatile heavy metals are not critical with regard to actual emission limits. They can be kept under control by an efficient dedusting.

According to comparatively secured information [1, [18 the emissions of As, Be, Co, Cr, Cu, Mu, Mo, Ni, P, Pb, Sb, Se, Te, V, Zn are extremely low on suspension preheater kilns with efficient dedusting. As a general rule the emission of non- or low-volatile elements is always much below 0.1% of the corresponding metal input into the suspension preheater kiln.

Thallium has a different behavior. It is known to form an outer cycle (not inside kiln) which can create a high accumulation in the filter dust (a few thousand times) if no countermeasures are taken. This can also increase the normal solid emission or become a potential danger as at Lengerich.

On grate preheater kilns not only Tl but also additional elements as Cd, Pb and Zn can become highly enriched in the filter dust. The emissions of all these elements are still mainly in solid form and therefore related to the efficiency of the filter. Due to the enrichment effects the emission may reach the order of 1% (instead of 0.1% as before).

All elements mentioned so far and under the conditions of suspension or grate preheater kilns are known to have a very low or insignificant vaporous proportion (equilibrium concentration). This is certainly applicable for exhaust gas temperatures  $<150^{\circ}\text{C}$ . It should be kept in mind that the volatility depends not only on the temperature but also on the other accompanying components occurring on cement kilns (e.g. Cl).

### **7.1.2 Volatile Metals**

Volatile elements cannot be controlled by efficient dust filters and are also classified as most toxic (class 1). Therefore, they need special attention.

The most prominent example is the mercury. Hg is suspected to be almost totally emitted [18, 24, 25]. At the same time the emission limit is only  $0.2 \text{ mg/m}^3$ , therefore, it may soon become critical if the Hg input is significant. Hg emissions on cement kilns are almost completely in form of vaporous Hg. Therefore, many older emission measurements (based on pure solid sampling) either omitted Hg or did show unrealistically low figures.

Although Hg is very volatile, a certain retention effect in the cement kiln system is also possible. This may e.g. be the case under the influence of some sulphur compounds or in a raw mill during compound operation [7]. However, the retention during mill operation creates a Hg accumulation which can evaporate when switching to direct operation thus creating a high peak emission and a less favorable long term retention effect. This was e.g. observed in [18] when some  $0.2 \text{ mg/m}^3$  were found during direct operation. However, this high emission value seems to be very exceptional in general because normal raw materials and fuels do not create critical Hg inputs. The problem of the highly volatile Hg is therefore limited to very special cases and is not a general problem under the present emission limits.

It is not quite clear whether also other elements could become as volatile as Hg under certain conditions. According to [14] Selenium on grate preheater kilns would be highly volatile but this is not confirmed.

### **7.1.3 Long Wet and Long Dry Kilns**

Unlike suspension and grate preheater kilns long wet and long dry kilns are less explored in their heavy metal emission behavior. From the basic principle and from the higher stack gas temperatures (high vaporous equilibrium concentrations) one could expect a less favorable situation but the practical evidence is incomplete.

The most complete and extensive information basis so far are heavy metal balances from the wet kiln at Obourg [16]. The results are partly surprisingly favorable. The emissions for all heavy metals investigated such as Be, Cd, Hg, Tl, As, Co, Ni, Se, Cr, Cu, Mn, Pb, Sn, V, Zn are very low and the calculated relative emissions are below 0.5% even for Cd, Tl, Hg. In other words: none of the heavy metals seems to be volatile. The elements of class 1 and 2 are typically  $< 0.01 \text{ mg/m}^3$  and class 3 elements are  $< 0.1 \text{ mg/m}^3$ .

## **7.2 Specification of Missing or Inaccurate Data**

When reviewing the corresponding literature one is often impressed by the very low heavy metal emission or the excellent metal retention effect found for certain elements. When going more into details it becomes evident that such impressive results are usually based on pure solid sampling on the clean gas. The vaporous proportions are also verified in some cases but the measuring methods on cement kiln exhaust gases do not allow for extremely low detection limits ( $< 1 \text{ mg/m}^3$ ) under practical conditions (method in [20] is not accepted for practical emission measurements).

Measuring methods for vaporous proportions of metals also appear as possible weak point in some cases. Measurements do often consider only solid sampling and the assumption is made that vaporous proportions are negligible. The analytical confirmation is often missing

due to the lack of sufficiently sensitive measuring methods. And if the dedusting performs very well, very low emissions and impressive retention effects for heavy metals of 99.999% or even better can be calculated. Although there seems to be no problem with respecting emission limits there could be a problem with the impressive number of nines in the retention effect. In view of vision towards a future "zero emission" sampling methods and analytical procedures need to be improved.

## **8. STANDARD TECHNOLOGY FOR REDUCTION OF HEAVY METAL EMISSION**

### **8.1 Reduction of Heavy Metals Input into Kiln System**

The input of heavy metals into the kiln system from raw materials and fuels can be controlled and limited in order to avoid undesired effects. The justification can be:

- ◆ Limits set for heavy metals in clinker (usually "political" limits, concentrations are often too low to produce clear negative effects in clinker, except Cr)
- ◆ Cycles of semi-volatile heavy metals and their influence on (CKD) kiln dust or bypass dust
- ◆ Emission of volatile heavy metals (e.g. Hg)

With regard to emissions, it is most important that the heavy metal input is limited, especially if conditions are present which promote emissions such as:

- ◆ high stack gas temperature
- ◆ low metal retention capacity of kiln system
- ◆ presence of compounds which can volatilize the metal, such as chlorine

For example, if sewage sludge is burnt in a cement kiln the measuring input has to be limited [18, 19].

The emission of a metal only becomes important if the metal cycle can actually reach the filter and if there is a problem with the function of the filter (EP shut down or poor performance), e.g. Thallium cycle on SP kiln

Besides these special cases most of the known heavy metals behave as low volatile and are virtually not emitted. The question is rather which metal concentrations in clinker and kiln dusts are acceptable from a political and environmental point of view. Therefore, input reduction will always maintain its importance, even if metal emission values are very low.

## **8.2 Modification of Process**

### **Break the Cycle of Enrichments**

If semi-volatile metals as e.g. Tl cannot be avoided in the raw mix there is a possibility to break the cycle of Tl enrichment. This will then limit the maximum concentration in the filter dust and thus reduce the potential risk during any malfunction of the filter.

The principle is often used on systems which originally worked with complete reintroduction of the kiln dust (closed systems), as e.g. suspension preheater kilns or grate preheater kilns without any bypass. Enriched filter dust is extracted from the system and usually introduced into the cement grinding process, e.g. on suspension preheater kilns in combination with a raw mill the kiln dust during direct operation can be extracted. The costs are very moderate (< 0.2 Mio CHF). The effects in terms of normal emission is not the main argument, it is rather a reduction of a potential risk.

## **8.3 Secondary Reduction Measures**

### **Improve Dedusting**

In case of non or semi-volatile heavy metals the emission can be reduced by improving or replacing the dedusting. The effect of an improved emission is an almost linear decrease of the heavy metal emission according to the reduction of the dust emission. However, the heavy metals are usually not the main justification for such modifications.



## **9. BAT (BEST AVAILABLE TECHNOLOGY) FOR REDUCTION OF HEAVY METAL EMISSION**

### **9.1 Non-volatile metals**

For most of the heavy metals which are non-volatile or semi-volatile the emission reduction can be achieved by reducing the dust emission (see paper PT 95/4391/E, dust).

### **9.2 Volatile metals**

Special technology in form of secondary reduction measures is only justified for volatile metals as e.g. Hg. The following technologies are possible:

- 1) Dry scrubbing by circulating fluidized bed is also effective for Hg reduction [26. The use of other absorbers (activated coke) is also possible and would improve the effect.
- 2) Activated coke filter The Polvitec at "HCB Siggenthal removes Hg at an efficiency of some 99%. As a pure Hg removal system it would be extremely expensive for this particular purpose (Investment of approx. 30 Mio CHF). Since the activated coke is re-used as kiln fuel the mercury would form a cycle. The cycle is broken up by extracting filter dust during direct operation and using it in cement grinding. Treatment of the dust (thermal Hg-expulsion) has been tested but not realized on a large scale due to low Hg concentrations.
- 3) Wet scrubbing This is not yet known on cement kilns but rather on waste incinerators. Wet scrubbing of mercury is inefficient if Hg is present in metallic form (insoluble) and may not be automatically the appropriate method [29. Oxidizing the Hg would be necessary. Again, this method would be extremely expensive only for the purpose to remove volatile heavy metals.
- 4) Removal of critical heavy metal from specific fuels or material components

Example: Hg can be thermally expelled from sewage sludge before feeding it into a cement kiln [27].

**10. LITERATURE**

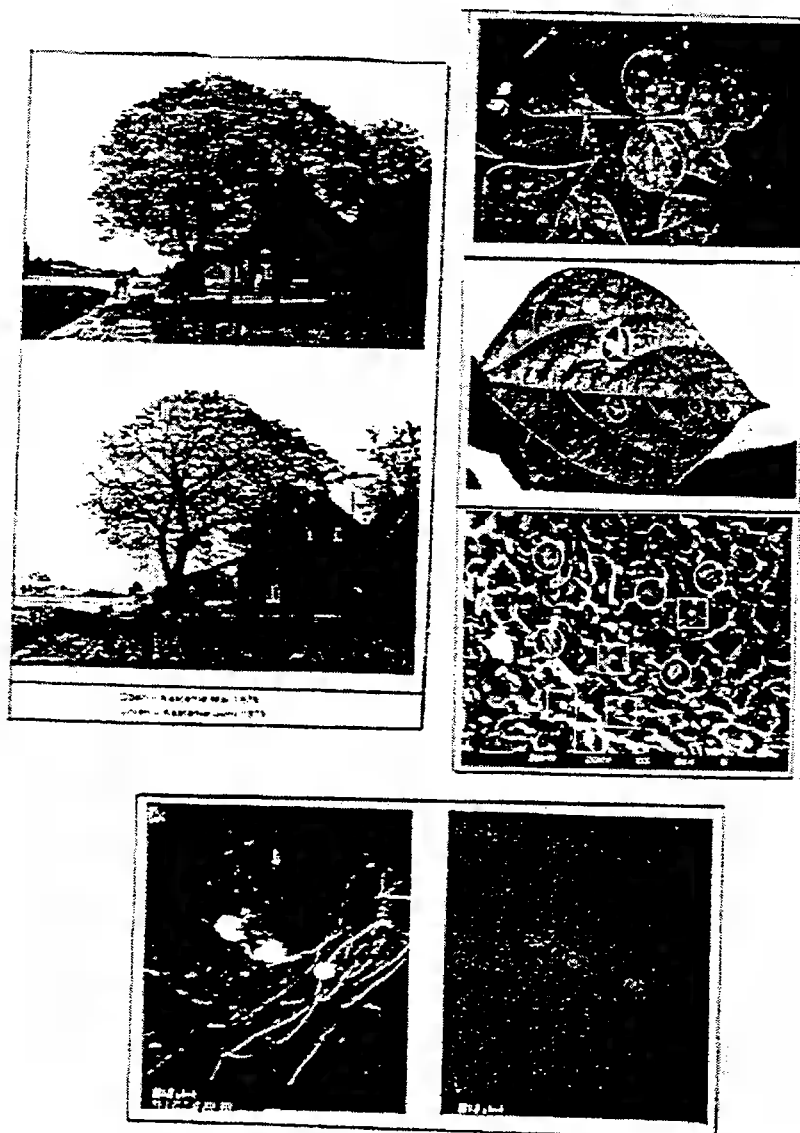
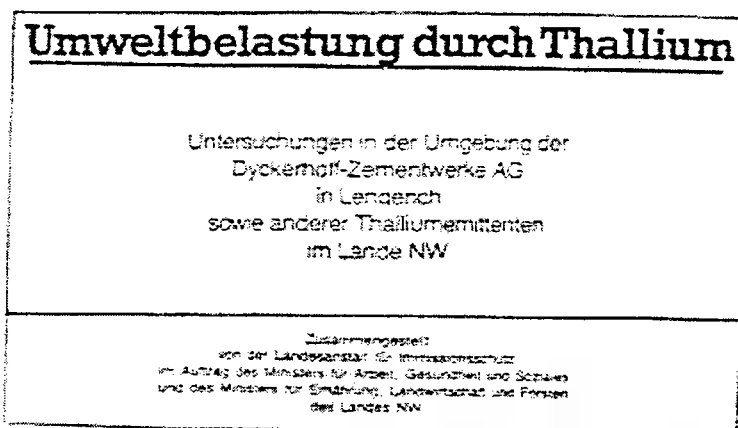
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## 11. APPENDIX

### 11.1 Thalium Documentation Dyckerhoff-Zementwerke AG, Lengerich



Characteristics of Toxic Elements quoted in TA Luft and LRV

Element	Class	Critical Dose		Uses	Source	Natural concentrations
		WHO max. dose	Lethal dose			
Cd	I	0.5 mg / week		Coating for metals (hot dip) Alloying material (wires, bearings, batteries) Pigment (CaS in glass, paints, etc.) Insecticide (CdO, Cd(OH) <sub>2</sub> )	Zn / Pb Ores	1 ppm in plant and animal tissues
Hg	I			Scientific instruments Mercury vapour lamps Solders Mercury arc rectifiers Anti-fouling paints Pharmaceuticals Seed dressing	HgS (Cinnabar)	Soils, dust, water, 0.005 - 0.25 ppm in nearly all foods
Tl	I		100 ppm poss. toxic to soils  12 mg/kg body weight	Rodenticide / insecticide (Thallous sulphate) Lenses, IR instruments Alloying material Fireworks Dyes, pigments Low temperature thermometer (with Hg) Catalyst Hair remover	Pyrites	Not naturally found in plants or soils
Be	I (cancer.)			Cu / Be alloys X-Ray tubes Fluorescence light tubes Nuclear reactor parts	Beryl ore	
As	II	MAC of 0.5 mg/m <sup>3</sup>		Insecticides, Weed killers, fungicide (as K-arsenate), Wood preservative Glass Alloying material Therapeutic (organic As compounds)	By-product Cu, Pb, Zn, Sn, Au-ores	In all soils from <10 to 500 ppm
Co	II		10-20 mg per 100 g body weight	Alloying material Magnet alloys Cutting tools Binder for tungsten carbide Blue pigment in china glass	In Cu / Co ores in Zaire	
Ni	II	Ni and soluble Ni-salts are not considered as being toxic to humans. The most important industrial aspect is their trend to cause dermatitis.		Alloying material Special steels Electroplating Catalyst for hydrogenation of oils Coinage Paints and enamels Ni-Cd batteries	S-ores in Ontario	0,0016% of the Earth's crust and is widely found in soils and plants
Se	II			Se rectifiers Anti-corrosive coating on copper, steel etc. Decolouriser in glasses Paints and dyes Photoelectric cells Insecticides Catalyst	Anode slime of Cu-refineries	II soils from trace to 30 ppm, at which level animals suffer from alkali disease
Te	II			In cast iron to improve properties In various Pb, Cu and Fe alloys In rubber industry As catalyst Glass colouring agent In bacteriological tests In thermocouples for low temperature	Bi-ore residues	Traces in seleniferous soils but not in crops

Element	Class	Critical Dose		Uses	Source	Natural concentrations
		WHO max. dose	Lethal dose			
Sb	II			Alloying material Battery grids Pewter Printers type Lead electrodes Bearing metals Rubber compounding Flameproof clothing Paint pigment In ceramic / glass	Sb <sub>2</sub> S <sub>3</sub> (Stibnite)	
Pb	III			Pipes, Roof coverings Tanks for acids Lead shot, Bullets, Linotype metal Battery plates Alloying material In paints and pigments In glasses and enamels Litharge rubber Insecticides Noise barriers	PbS (Galena)	In soils and plants in very low levels. Clay soils make Pb insoluble but acid soils increase solubility and toxicity.
Cr	III			Alloying material in steels Chromium plating Cutting tools (as carbide) Paint primer (zinc chromate) Leather tanning agent Wood preservative (zinc, chloride, chromate) Pigment (paint, inks, dyes, etc.) In photo industry as sensitiser	FeO.Cr <sub>2</sub> O <sub>3</sub> (Chromite)	In small quantities in all plants and soils. Plants grown on soils with 0.2-0.4% are infertile
CN	III					
F	III					
Cu	III		780 mg as CuSO <sub>4</sub>	Alloying material As electrical conductor Gas / water pipes, Roof sheeting Bronze paint Anti-fouling paint Insecticide	As S-ores in several areas	
Mn	III			Alloying material Potassium permanganate Colour in glasses / ceramics Paints, inks Matches, Fireworks Enrich manganese deficient soils	As oxide sulphide and carbonate	up to 20 ppm in some nuts
Pd	III			Alloying material Catalyst Dental alloys Jewellery	In certain coals as arsenide or selenide	
Pt	III			Contact material in electrical circuits Electrode material Catalysts High temperature electric furnaces Dies for glass fibre production	As native metal in Cu / Ni ores	
SiO <sub>2</sub>	III					
Rh	III			Pt / Rh alloys Electroplating Electrical contacts surfaces Reflector in high power lamps	In wastes from Cu, Ni and Pt extraction	

Element	Class	Critical Dose		Uses	Source	Natural concentrations
		WHO max. dose	Lethal dose			
V	III			In special steels and alloys Industrial catalyst Pigment in paints, dyes, inks In insecticides In photography	Oil refinery residues (Camotite)	To 470 ppm in soil; to 10 ppm in plants
Sn	III					

